 #5

and the three roots of the equation are

$$2h, \quad h-3k, \quad h+3k \text{ respectively,}$$

and are therefore all rational.

Here it may be observed that the condition of R being an even number, which we know, *à priori*, is the case when all the roots are rational, is involved in the two more general conditions already expressed. It will now be evident that the first condition by no means involves the second, as it is perfectly easy to satisfy the equation $f^2+3g^2=Q^3$ without supposing anything relative to k, the common measure of f, g, Q, except that it be itself of the form $\lambda^2+3\mu^2$, which will give

$$\left(\frac{f}{k}\right)^2+3.\left(\frac{g}{k}\right)^2=(\lambda^2+3\mu^2)(r^2+3s^2)^3,$$

an equation which can be solved in rational terms for all values of λ, μ, r, s; and consequently the product of the squares of the differences of the roots may be a square, and at the same time the roots themselves may be irrational *.

I believe it will be found on inquiry that the equation $x^n-qx+r=0$ will always have two *rational* roots if

$$(n-1)^{n-1}.q^n-n^n.r^{n-1}$$

be a complete square, provided that q be prime to r.

Furthermore, viewing the striking analogy of the general nature of the conditions of rationality already obtained, to those which serve to determine the reality of the roots of equations, I am strongly of opinion that a theorem remains to be discovered, which will enable us to pronounce on the existence of integer, as Sturm's theorem on that of possible roots of a complete equation of any degree: the analogy of the two cases fails however in this respect, that while imaginary roots enter an equation in pairs, irrational roots are limited to entering in groups, each containing *two* or MORE.

4 Park Street, Grosvenor Square,
November 7, 1844.

LXXV. *On some Photographic Phænomena.* *By* George Shaw, *Esq.*† #560·2

IT is well known that the impression produced by light on a plate of silver, rendered sensitive by M. Daguerre's process, is wholly destroyed by a momentary exposure of the

* Thus then it appears that the *total* rationality of the roots of the equation $x^3-qx-r=0$ may be determined by a direct method without having recourse to the 0 method of divisors to determine the roots themselves; the two conditions being that 49^3-27r^2 shall be a perfect *square*, and the greatest common measure of q^3 and r^2 a perfect *sixth* power.

† Communicated by the Author.

plate to the vapour of either iodine or bromine. Although this fact has long been known, the nature of the action by which so extraordinary an effect is produced, has not yet been satisfactorily explained. In the hope of elucidating this subject, a series of experiments was instituted, the results of which are recorded in the following remarks.

In order to prevent misapprehension, as well as to avoid circumlocution, it will be well, before proceeding to the experiments, to describe very briefly the various stages of the process by which the sensitive surfaces employed, were prepared. A smooth surface of pure silver plated upon copper is rendered perfectly clean, and is at the same time highly polished by being rubbed or scoured with a mixture of powdered tripoli and dilute nitric acid; the mixture being applied to and rubbed about the plate by a pledget of cotton wool. When the plate has been sufficiently treated in this way (the time required for which can only be determined by experience), the mixture is removed by pledgets of dry wool. The polish of the surface is still further improved by buffing the plate with a buff of clean cotton velvet on which fine charcoal powder has been sprinkled. The surface of a plate of silver thus treated is highly polished, and is assumed to be perfectly free from foreign matter. In order to render such a plate sensitive to light, it is supported over a vessel containing iodine, the silver surface being of course downwards. The vapour of iodine immediately attacks the surface of the silver, and forms, by combining therewith, a stratum of iodide of silver. By removing the plate from time to time and examining it by a feeble light, the relative thickness of the film of iodide of silver may be ascertained by its colour. The plate at first has a yellow colour, which by further exposure passes to a deep gold, to an orange, and next to a purple or rose colour; by still further exposure it becomes blue, and passes through a series of other colours; but as the purple or rose colour indicates that thickness of the film of iodide of silver most favourable to photographic experiments, it will be unnecessary to follow the plate through the changes consequent upon further exposure. This preparation of the silver plate is performed in a room from which daylight is excluded, or into which it is only partially admitted, for the purpose of examining the colour of the plate.

The film of iodide of silver thus procured is very sensitive to light, but may be made more so by exposure to the vapour of either chlorine or bromine. The quantity of either of these vapours necessary to communicate the maximum sensitiveness to the iodized plate is exceedingly small; and the pre-

sence of a larger quantity produces a state of insensibility to light. In order to determine the absorption of the proper quantity of the vapour of bromine (for bromine, from its superiority, is now used to the exclusion of chlorine), a very dilute solution of bromine in water is introduced into a glass vessel, and the iodized plate is suspended over it for a time varying according to the strength of the solution and the temperature, and which can be determined only by experiment. Instead of the treatment described, other processes may be resorted to for the preparation of the plate; a solution of chloride of iodine alone communicates sensitiveness to a silver plate, without a previous exposure to iodine; and instead of pure chlorine or bromine, the chloride of bromine, or bromide of iodine, may be used after the iodine. These, and various other accelerating substances, have been proposed, and are used by different experimenters; but they all contain chlorine or bromine, or both, and differ from each other only in the ingredients in which they (the active agents) are disguised. In the experiments hereafter related, it must be borne in mind, that although iodine and bromine are alone mentioned, and were for the most part used, yet the same results have been obtained by the use of all the accelerating agents enumerated, as well as several others.

A silver plate prepared by the process described, may be exposed to the vapour of mercury without being in any way affected by the exposure. If however the prepared plate be previously exposed to light, or made to receive the luminous image formed in the *camera obscura*, the mercurial vapour attacks it; forming, in the former case, a white film, and in the latter, a picture corresponding to the luminous image which had been allowed to fall on it.

If a prepared plate after receiving a vertical impression by light be exposed to the vapour of iodine or bromine, it is found that the vapour of mercury no longer attacks it; or, in other words, the impression produced by light is destroyed.

The first experiments made for the purpose of arriving at the cause of this phænomenon, had reference to the relation between the time of exposure to light and the time of exposure to the vapour of iodine or bromine necessary to destroy the effect produced by light. Prepared plates were exposed in the *camera obscura* for a length of time, which previous experiment had determined to be sufficient for a full development of the picture; some of those plates were exposed during two seconds to an atmosphere feebly charged with the vapour of bromine, while others were carefully preserved from contact with the vapours of iodine or bromine. The atmosphere

of bromine employed was produced by adding thirty drops of a saturated solution of bromine in water to an ounce of water; the solution was poured into a glass vessel, and the plate was exposed to the vapour in this vessel during the time specified. The plates were then introduced into the mercury box, and by volatilizing metal, the pictures were developed on all those which had not been exposed to the vapour of bromine, while those which had been exposed to it exhibited no trace of a picture under the action of mercury.

The same experiments were repeated with iodine, with exactly similar results.

Prepared plates were exposed to diffused light in the shade, and others were exposed to the direct rays of the sun; the object being in both cases the production of a more intense impression than that produced by the feeble light of the *camera obscura.* Some of these plates were exposed to the vapour of bromine, and others to the vapour of iodine, while others were carefully preserved from the vapours of these substances. On subsequent exposure to the vapour of mercury, those plates which had not been exposed to iodine or bromine exhibited, by the large quantity of mercury which condensed on them, the effects of exposure to intense light; while those which had been subjected to the action of either bromine or iodine, were in no way affected by the vapour of mercury. Many repetitions of these experiments demonstrated that the effect of exposure to the most intense light was completely destroyed by the shortest exposure to the vapour of bromine or iodine.

Experiments were now instituted for the purpose of ascertaining in what condition the prepared plate was left after having been first exposed to light and afterwards exposed to the vapour of bromine or iodine. In these experiments a method of treatment somewhat different from and more convenient than that described, was resorted to, as in practising that method effects occasionally presented themselves which interfered with the results, and rendered it difficult to determine with certainty how far some of the appearances produced were due to the action of light. It has already been stated, that a prepared plate has a maximum sensitiveness when the iodine and bromine are in a certain relation to each other; if there be a deficiency of bromine, the maximum sensitiveness is not obtained, and, if there be an excess, the plate is no longer sensitive to light; but when exposed to the vapour of mercury, *without having been exposed to light*, becomes white all over, by the condensation of mercury thereon; that is to say, it exhibits the appearance of a plate which had

been *properly* prepared, and which *had* been exposed to light. From this it will be evident, that a plate properly prepared in the first instance, and then exposed to light, may, by subsequent exposure to the vapour of bromine, have the impression produced by light *wholly destroyed*; and yet, by the accumulation of bromine may exhibit, on exposure to mercury, an appearance similar to that due to light. In other words, it is impossible (in the case supposed) to distinguish between an effect produced by light and an effect due to excess of bromine. By using iodine in place of bromine, there is no risk of producing the appearance which accompanies excess of bromine; but on the other hand, by augmenting the quantity of iodine, the sensitiveness of the plate is diminished. These difficulties were overcome by using a solution containing both iodine and bromine, in such proportions that the evaporation of each should take place in the proportion in which they produce on silver the most sensitive surface. The solution employed was made by adding alcoholic solution of iodine to a solution of chlorate of potash until the latter would take up no more of the former, and to each ounce, by measure, of this solution ten drops of a saturated solution of bromine in water were added. The solution of chlorate of potash was made by diluting one part of a saturated solution of the salt with ten parts of water. The use of the chlorate is simply as a solvent of iodine. In the subsequent experiments the plate was exposed to the vapour of this mixture of iodine and bromine with precisely the same effect as when either was used separately, and without the inconvenience or uncertainty which attended their use.

A number of preliminary experiments, the detail of which would be uninteresting, appeared to indicate, that not only is the effect of light on a Daguerreotype plate destroyed by iodine or bromine, but that the plate is restored to its original condition; in other words, that its sensitiveness to light is restored. In order to determine this point, the following experiments were made.

A prepared plate was exposed to light, and afterwards to the mixed vapour*; mercurial vapour produced no effect upon it after a long exposure; the plate on removal from the mercury box was a second time exposed to light, and again introduced into mercurial vapour. The appearance of the plate was very little changed, and it was concluded that no effect, or, if any, very little, was produced by the second ex-

* I shall hereafter call the mixed vapours of iodine and bromine produced in the way described in the last paragraph but one, *mixed vapour*, in order to avoid circumlocution.—G. S.

posure to light. This conclusion was, however, erroneous, as the following experiments prove.

A prepared plate was exposed to light, and afterwards to the mixed vapour; mercurial vapour was found to have no effect upon it; the plate was then partly covered with a metallic screen, fixed close to but not in contact with it, and the whole was exposed to light. On placing the plate in the mercury box, a broad white band, nearly corresponding to the edge of the defended part, made its appearance; the whole of the defended part (excepting the band in question) was unaffected, and the exposed part exhibited very little change. By a careful examination of the plate after it was removed from the mercury box, the white band in the middle appeared to be produced by the feeble light which had passed under the edge of the metal plate which had screened the light from part of the prepared surface; and the very dark, and apparently unaltered appearance of the exposed part, was occasioned by an excess of action, for mercury was found to have condensed on that part in large quantity, and to have produced the dark lead colour which is commonly called *solarization*; but which effect, in the case in question, was so excessive, that the colour of the part on which mercury had condensed differed but very slightly from that on which no light had fallen. It was now evident that the apparent absence of effect in the last experiment was in reality occasioned by an excess of action; and by repeating that experiment, and making the time of the second exposure to light much shorter than before, the plate assumed, under the action of mercury, an intense and beautiful whiteness.

From these experiments, then, it was perfectly clear that the impression produced by light on a Daguerreotype plate is wholly destroyed by the mixed vapour, and that *its sensitiveness to light is restored.*

It now remained to discover to what extent the sensitiveness is restored by the treatment in question. It was not at first expected that the sensitiveness to light was as great after this treatment as after the original preparation of the plate; but experiment afterwards proved that the surface lost none of its sensitiveness by this treatment, nor even by numerous repetitions of it. A prepared plate was exposed to light; the impression was destroyed and sensitiveness restored by the mixed vapour; the plate was a second time exposed to light and a second time to bromine, still its sensitiveness appeared unimpaired; for a fourth or fifth exposure gave, on treatment with mercurial vapour, a vivid impression. In order to determine with the greatest accuracy if the sensitiveness

of the prepared surface was at all impaired by these repeated exposures to light, the *camera obscura* was resorted to. A series of plates was prepared with the utmost attention to uniformity; some of these were exposed in the *camera obscura*, and pictures obtained by the subsequent exposure to vapour of mercury; the time requisite for the proper development of the picture was noted; others were first exposed to the direct rays of the sun, and afterwards to the mixed vapour, and these were exposed in the *camera obscura* for the same length of time as those which had not been exposed to light. On treatment with mercurial vapour perfect pictures were produced, which could not be distinguished from those taken on plates prepared by the ordinary method. So completely does the mixed vapour restore the sensitiveness of prepared plates after exposure to light, that the most beautiful impressions were obtained in the *camera obscura* in two seconds on plates which had previously been *four* times exposed to the direct light of the sun, and after each such exposure treated with the mixed vapour.

As the plates experimented on, to this stage of the inquiry, had been *wholly* exposed to the sun's light previous to exposure in the *camera obscura*, it was thought that possibly some slight effect was produced, which, from being the same on all parts of the plates, escaped observation; and in order to avoid the possibility of error from this cause, the impressions of light which it was intended to destroy by bromine were afterwards made in the *camera obscura*. Prepared plates were impressed with virtual images of different kinds, the *camera obscura* being pointed first at a house, afterwards to a bust, next to a tree, and finally to a living figure, the plates after each impression, excepting the last, being momentarily exposed to the mixed vapour. In every instance the most perfect impressions of the objects to which the *camera obscura* was last directed were obtained, and no trace of the previous impressions was left.

Experiments were next instituted for the purpose of ascertaining if the prepared surface, *after* the process of mercurialization, could be made to receive another impression by treatment with mixed vapour. Impressions were taken with the *camera obscura*, and after the full development of the picture by vapour of mercury, the plates were exposed to bromine and again placed in the *camera obscura*, the instrument being directed in the different experiments to different objects; on exposure to mercurial vapour other pictures made their appearance, and although confused from superposition on the first pictures, could be clearly traced, and were found

perfect in every part. This production of picture upon picture was repeated, until by the confusion of the superposed images the effects of further exposure could be no longer distinguished.

In all the experiments hitherto described the destruction of the impressions by bromine was effected in the dark, the apparatus being situated in a room into which only a very feeble daylight was admitted. It remained to be discovered if the mixed vapour had the power of destroying the effect of light while the plate was still exposed to light, or if the vapour had the power of *suspending* or *preventing* the action of light on a Daguerreotype plate. In order to determine this point, the apparatus was placed near the window of a well-lighted room, and so arranged, that during the whole time of the preparation of the plate, by exposure first to iodine and afterwards to bromine, it was exposed to full daylight, and by a mechanical arrangement, of too obvious a nature to render description necessary, the plate was withdrawn from the bromine vessel into a dark box; that is to say, it was withdrawn at the *same moment* from the influence both of light and bromine: on being placed in the *camera obscura*, plates so prepared received impressions, which by mercurialization produced excellent pictures, and there was no trace of the action of any light save that of the *camera obscura*. It follows then that light is incapable of exerting any appreciable influence on Daguerreotype plates during the time they are receiving their coatings of iodine and bromine.

Although these experiments afford no information on the subject in reference to which they were originally undertaken, they are yet not without interest, both in their theoretical bearing and in their practical application. They demonstrate not only that the change (whatever it may be) effected by light on silver plates prepared by Daguerre's process is completely suspended in the presence of the vapour of either iodine or bromine, but that after that change has been produced the impression may be destroyed and the plate restored to its original condition by a momentary exposure to either of these vapours. In their practical application these experiments show, that all the care which has been taken to exclude light from Daguerreotype plates during their preparation is unnecessary; that so far from a dark room being essential to the operations of the Daguerreotype artist, the light of day may be allowed to fall on the plate during the whole time of its preparation; and that it is only necessary to withdraw it at the same moment from the action of bromine and light by sliding it from the bromine vessel into the dark box in which it is carried to the *camera*

obscura; and where, from situation or otherwise, there is a difficulty in observing the colour of the plate during the process of iodizing, it may be removed from the iodine vessel and its colour examined by the direct light of the sun without risk of injury; for when returned to the iodine or bromine vessel for a moment the effect of light is wholly destroyed.

Perhaps the most valuable practical application of these facts is in the use of the same plate for receiving several impressions. When, on taking a portrait or the picture of any object liable to move, there is reason to suppose that the motion of the person or object has rendered the operation useless, it is not necessary to throw aside the plate on which the imperfect impression has been taken, and resort to the tedious process of cleaning and preparing another; it is only necessary to treat the plate in the manner already pointed out, and it is again equal in every respect to a newly prepared plate; and this treatment may be repeated until by the slow accumulation of too thick a film of iodide of silver, the plate no longer possesses the same degree of sensitiveness to light.

Temple Row West, Birmingham, GEORGE SHAW.
November 15, 1844.

LXXVI. *On the Constitution of the Urine in Man and Carnivorous Animals. By* JUSTUS LIEBIG, *M.D., Ph.D., F.R.S., M.R.I.A., Professor of Chemistry in the University of Giessen**.

IT is a very curious and remarkable fact that all the analyses and examinations hitherto made of the urine of man and of carnivorous animals have not yet afforded us any satisfactory answer to the question, What is the substance which imparts to that fluid its property of reddening blue vegetable colours?

In most physiological and chemical works we find the acid reaction of urine ascribed either to uric acid or to lactic acid; but no positive and definite proof is given of the presence of the latter acid in urine.

The acidification of milk, that is, the formation of lactic acid, is dependent upon the milk-sugar contained in milk; this substance being in contact with caseine in a state of decomposition and transformation, undergoes, by its means, an alteration, which consists in its elements transposing and arranging themselves into lactic acid without the addition or separation of any one atom. Crystallized milk-sugar ($C_{12} H_{12} O_{12}$) and hydrate of lactic acid ($C_6 H_6 O_6$) have one and the same

* From the Lancet, Nos. xi. and xii., by the obliging permission of T. Wakley, Esq., M.P.